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# <Division of Synthetic Chemistry>Organoelement Chemistry

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# Division of Synthetic Chemistry – Organoelement Chemistry –

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## Scope of Research

Organic chemistry has mainly developed with the use of second-row elements such as carbon, oxygen, and nitrogen, while the synthesis and isolation of the heavier congeners of typical organic molecules as stable compounds has been a dream for organic chemists. Our main research interest is the elucidation of the similarities and differences in structures and reactivities between organic compounds and the corresponding heavier congeners. These studies are interesting and important from the standpoints of fundamental chemistry, and open the way to the more extensive application of main group chemistry.

### KEYWORDS

Steric Protection  
Kinetic Stabilization  
Low-coordinated Species  
Heteroatom  
Transition Metal Complexes



## Selected Publications

Fujimori, S.; Mizuhata, Y.; Tokitoh, N., A Mixed-anion System Consisting of a Germyl Anion and Anions Delocalized on Conjugated Carbon Ring Skeletons, *Chem. Eur. J.*, **25**, 6284–6289 (2019).

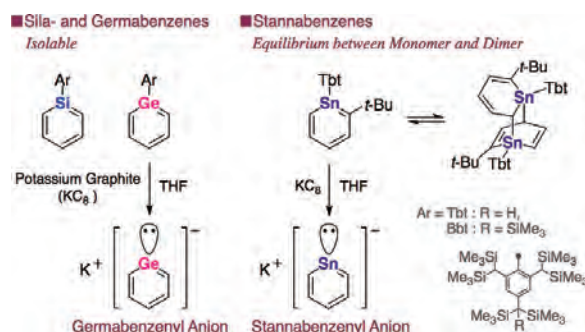
Yanagisawa, T.; Mizuhata, Y.; Tokitoh, N., Syntheses and Structures of Novel  $\lambda^3\lambda^3$ -Phosphanylalumanes Fully Bearing Carbon Substituents and Their Substituent Effects, *Inorganics*, **7**, 132–143 (2019).

Sugahara, T.; Sasamori, T.; Tokitoh, N., The Formation of a 1,4-Disilabenzene and its Isomerization into a Disilabenzvalene Derivative, *Dalton Trans.*, **48**, 9053–9056 (2019).

Sugahara, T.; Guo, J.-D.; Hashizume, D.; Sasamori, T.; Tokitoh, N., Reversible Isomerizations between 1,4-Digermabenzenes and 1,4-Digermadewar-benzenes: Air-stable Activators for Small Molecules, *J. Am. Chem. Soc.*, **141**, 2263–2267 (2019).

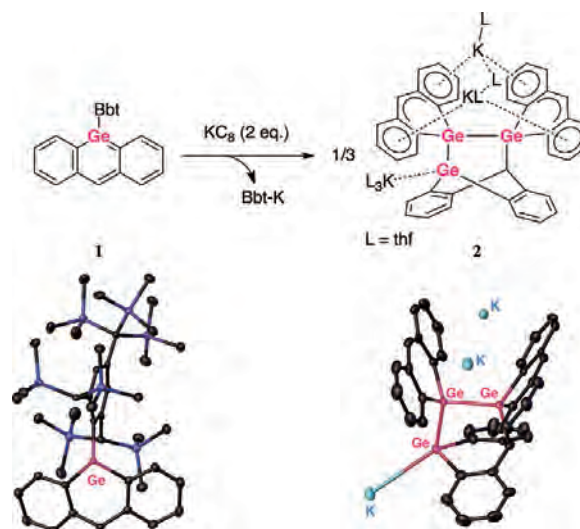
## Heavy Aryl Anion Species

“Heavy benzenes” in which the carbon atom(s) of the benzene ring is replaced by high-period group 14 element(s), *that is*, “heavy element” (silicon, germanium, tin, and lead), have attracted much attention from the interest of its aromaticity experimentally and theoretically. However, these compounds are extremely high-reactive species, *e.g.*, silabenzene ( $\text{HSiC}_5\text{H}_5$ ) in which one of the skeletal carbon atom of the benzene ring is replaced by a silicon atom, is known to decompose by self-oligomerization reaction even at very low temperature of  $-200\text{ }^\circ\text{C}$ . We have already succeeded in the synthesis and isolation of sila- and germanbenzenes as stable compounds even at room temperature by taking advantage of kinetic stabilization afforded by a very bulky substituent, Tbt group, to prevent the self-oligomerization. These compounds are found to have “aromaticity” and unique electronic state. In addition, recently, we successfully synthesized the germa- and stannabenzeylanions, the heavier Group 14 element ( $\text{E} = \text{Ge}, \text{Sn}$ ) analogues of phenyl anion as an isolable compound by the reaction of the corresponding isolated neutral germa- or stannabenzene having a Tbt group on the germanium or tin atom with potassium graphite ( $\text{KC}_8$ ).



In this study, utilizing the successful method of synthesis of the germa- and stannabenzeyl anion, we have reported the reduction of the previously reported 9-germaanthracene, resulting in the formation of a mixed trianion, the trimer of 9-germaanthracenyl anions. The reaction of 9-germaanthracene **1** with 2 equivalents of potassium graphite in benzene at room temperature led to the elimination of Bbt group as benzylpotassium, BbtK, together with a purple precipitate. Washing the reaction mixture with *n*-hexane and benzene followed by extraction with THF gave the trianion **2**, a trimer of the 9-germaanthracenyl anion, as a purple solid. The isolated trianion was characterized by X-ray crystallographic analysis, NMR spectroscopy and theoretical calculations. A trianion consisting of one germynyl anion and two anions delocalized on conjugated carbon ring skeletons was synthesized by trimerization of the

germanium analogue of the anthryl anion, which exhibits high germylene character.



## Novel Phosphanylalumanes

The bonding between group 13 (E) and group 15 (Pn) elements formulated as  $\text{R}_2\text{E}-\text{PnR}_2$  have attracted much attention due to their relationship, including the vacant p orbital on E and the lone-pair electrons on Pn. In this study, we have reported synthesis of novel  $\lambda^3, \lambda^3$ -,  $\lambda^4, \lambda^4$ - and  $\lambda^4, \lambda^3$ -Phosphanylalumanes **3-5**, Al-P single-bond species, by the reactions of aluminum monohalides [ $(t\text{-Bu})_2\text{AlBr}$  and  $(\text{C}_6\text{F}_5)_2\text{AlCl}$  0.5(toluene)] with  $\text{Mes}_2\text{PLi}$ . Substituent effects on an Al atom were investigated, and the introduction of  $\text{C}_6\text{F}_5$  groups on the Al atom substantially increased the Lewis acidity of aluminum. Based on the results of X-ray crystallographic analysis, theoretical calculations, and the reaction with benzophenone,  $\lambda^3, \lambda^3$ -phosphanylalumane **3** was found to have a well-separated vacant p orbital on an Al atom and lone pairs on a P atom. Further studies on the reactivity of phosphanylalumanes are now under way.

